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Exchange interactions of paramagnetic spins on α -Al₂O₃

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Introduction

Superconducting qubits (SQs) represent a promising route to achieving a scalable quantum computer.[1, 2] However, the coupling between SQs and (as yet largely unidentified) parasitic noise sources has so far limited the functionality of current SQs by reducing the coherence time of the quantum states below a practical threshold for measurement and manipulation.[3] These noise sources also more generally limit the performance of a variety of devices based on superconducting circuits, including high energy-resolution cryogenic radiation detectors, sensitive magnetic detectors (superconducting quantum interference devices, or SQUIDs), nanomechanical motion sensors and quantum-limited parametric amplifiers.[4-8]

Magnetic flux noise with an approximate $1/f$ spectral density is known to be one of the dominant contributors to loss of fidelity in both SQUIDs[9] and SQs.[10, 11] A number of experimental studies[10, 12] clearly implicate surface spins as a significant contributing factor to this noise. Recent work has shown that bare hydroxyl (OH) chemisorbed on the sapphire (0001) surface is a local paramagnetic center.[13] These OH defects on sapphire can serve as a physical model for spin centers on surfaces.

Excess low-frequency flux noise is a ubiquitous phenomenon observed in superconducting quantum interference devices (SQUIDs) and flux and phase qubits down to arbitrarily low temperatures. Various experiments have shown that flux noise has almost sample-independent properties: the power spectrum at low frequencies scales as $1/f^\alpha$ with $\alpha \sim 1$, and amplitude of order $1\mu_0 \text{ Hz}^{-1/2}$ at $f=1 \text{ Hz}$, where $\mu_0 = h/2e$ is the flux quantum. Understanding the mechanism producing this $1/f$ flux noise and developing strategies to reduce it are crucial steps towards improving the performance of superconducting devices in quantum information processing and for many applications of SQUIDs in, e.g., medicine and metrology. Recent experiments suggest that the observed flux noise is produced by the slow dynamics of paramagnetic spins localized on the surface. It has been proposed that interactions among spins leading to spin-clusters of various sizes can explain to the $1/f$ nature of observed flux noise, if the different clusters exhibit different spin-flip dynamics.[14]

For spins close to a metal/superconductor, the spins may interact via the isotropic long-range RKKY interaction. Similarly, “RKKY-like” interactions are possible for spins interacting through a non-metallic substrate. In addition, spins can couple directly via dipole-dipole interactions, which are anisotropic and depend on the relative spin orientations and magnitudes. Spin clusters may favor ferromagnetic (FM), antiferromagnetic (AFM), or spin glass ordering, which affects the noise characteristics. Random distances among spins leads to competition between FM and AFM domains, and motion of phase boundaries between them, as a source of $1/f$ noise. In this paper, we study the origins of spin interactions on a

substrate using OH on sapphire as a model system. We show how the substrate can mediate spin-spin interactions generally favoring FM interactions, but that strain can modify the interaction. Surface and sub-surface defects between the spin defects may also enhance the exchange interactions.

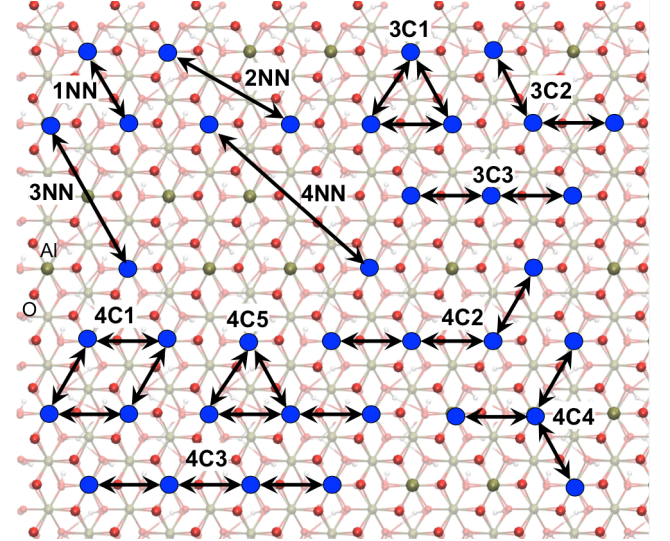


Fig 1. Schematic top view of the α -Al₂O₃ surface. Four different nearest neighbor distances are shown as 1NN, 2NN, 3NN and 4NN.

Methods

We have modeled the α -Al₂O₃ (0001) surface using a slab consisting of four layers of the oxygen plane.[13] A 6x6 supercell (684 atoms and 3348 electrons) was constructed with at least 12 Å of vacuum space to prevent interactions between periodic images. While one side has a clean surface termination, the opposite side is terminated with hydrogen to maintain the charge balance of bulk sapphire. Further details of our simulation methods are provided in the supporting information (SI). Figure 1 shows four different nearest neighbor (NN) distances where surface magnetic moments can be induced. Our previous study has shown that extrinsic defects such as OH sitting on those sites can lead to induced localized surface magnetic spin by direct tunneling. Four different distances are labeled as 1NN (4.64 Å), 2NN (8.13 Å), 3NN (9.60 Å), and 4NN (12.56 Å). We also consider the case of spin clusters by putting multiple OH groups at the NN distances. Three different structural arrangements formed by three OH adsorbates are shown as 3C1, 3C2 and 3C3 in the order of the most to the least energetically favorable arrangement. Similarly, five different arrangements (4C1~4C5) shows clusters formed by four surface OH adsorbates in the order of the most to the least energetic preference.

To evaluate the interaction between two magnetic states, we calculate the exchange coupling parameter J between the two paramagnetic states as a function of distance. In this regard, the correspondence between the collinear spins of a

Heisenberg model is taken into account. From the Hamiltonian of a Heisenberg spin dimer, the exchange parameter J can be obtained by the energy difference between two oppositely aligned spin states: (See SI for more details)

$$J = (E_{AFM} - E_{FM}) / 2, \quad (1)$$

where E_{AFM} and E_{FM} represent the total energy of antiferromagnetic (AFM) and ferromagnetic state (FM) from the spin-polarized DFT calculations. For any given system, positive (negative) J value represents that FM (AFM) is the ground state. A high J value, resulting from large difference in energy between FM and AFM states, indicates that two magnetic states are strongly coupled and so act like a single spin cluster. In contrast, a low J indicates that two magnetic moments are decoupled and thus lead to an independent noise mechanism into the SQ. Our previous study has suggested that single paramagnetic spins associated with OH on sapphire can contribute to $1/f$ noise.[13] In this letter, we further discuss how multiple surface spins can interact with each other and behave as clusters with varying magnetic fluctuation properties under different conditions, such as geometry, clustering and strain.

Results

We first investigate interaction energetics to understand the preference of cluster formation between two OH-induced surface magnetic spins. Figure 2(a) shows the variation of interaction energy as a function of the distance between two OH groups. Four distance points indicate the first four different NN arrangements as shown in Figure 1. Our DFT calculations predict that surface OH groups preferentially cluster at the α -Al₂O₃ surface. The energetic preference of the 1NN arrangement is 42.09 meV compared to the non-interacting system. As the separation distance increases, the interaction energy rapidly decreases and reaches non-interacting states at 4NN arrangement; the interaction energy of 2.73 meV at the 2NN is disappeared at the 4NN arrangement. Thus, our energetic study show that the interactions between surface OH groups can be negligible when they are separated more than two atomic unit-cells distance (~ 10 Å).

We now discuss how the coupling strength of the induced magnetic moments varies with the separation distance of two OH groups. The magnetic coupling strength is estimated by calculating the exchange interaction parameter J as described above. Figure 2(b) shows the variation of J as a function of the distance. Similar to the interaction energetics, the coupling strength also decreases rapidly with the separation distance and vanishes at the 4NN. The exchange interaction of 13.54 meV for 1NN drops below 0.1 meV when the two OH-induced moments are separated by more than 10 Å. (We note that the energy scale of 0.1 meV is below the accuracy limit of our calculation method.) We further examine the effect of spin cluster on the variation of the magnetic exchange interaction. For this study, we constrained our calculations to the triangular arrangement of three OH groups (3C1), among the various cluster geometries. The blue symbols in Figure 2(b) show the variation of the J for a spin near the triangular cluster, as a function of the fourth spin's distance from the cluster. The

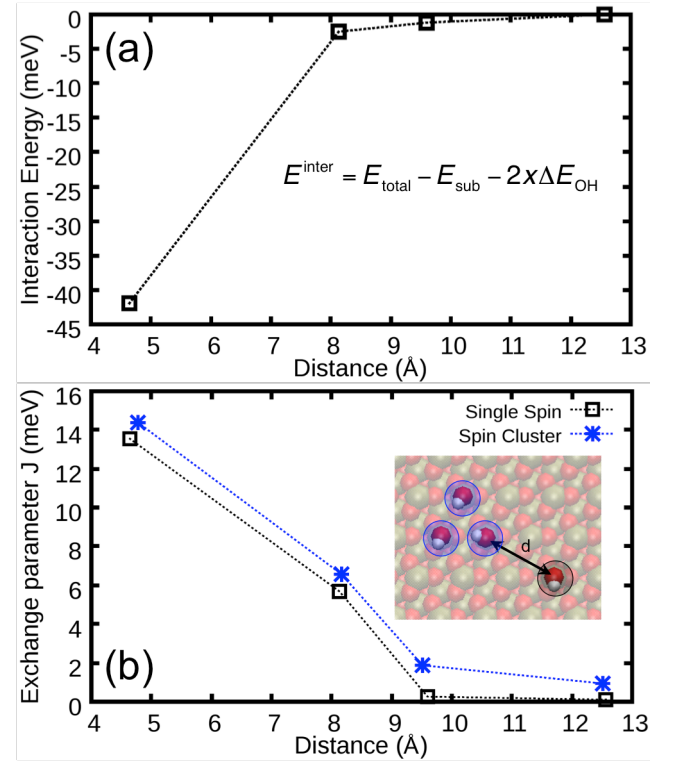


Fig 2. (a) Interaction energy between two OH-induced magnetic moments as a function of the separation distance. (b) Exchange parameter (J) of a OH-induced magnetic moment as a function of the separation distance from a single spin (black) or a spin cluster (blue).

separation distances are determined by considering the distance between a single flipping spin and the closest spin in the spin cluster. Our study shows that the formation of spin cluster enhances the magnetic coupling with a neighboring spin (evidenced by the blue symbols being higher than the black symbols for single spin interactions). This can be understood from the higher magnetic moment of the spin cluster enforcing strong ferromagnetic alignment on the interacting spin and thus increases the magnetic coupling strength. As a result, the distance of the spin-spin interaction is slightly extended. In other word, the coupling strength and distance between the interacting magnetic spins are dependent of the size of magnetic moments of each component. Thus, the magnetic coupling strength is dependent on both the size of ordered magnetic clusters and the distance between the moments. We note here that the magnetic coupling strength also shows some site dependence, since redistribution of spin density can change the spin-spin or the spin-cluster interaction.

Our study on the spin-cluster interaction showed that the formation of spin cluster could enhance the coupling strength with a nearby spin. We now focus more on the geometric dependence of the magnetic coupling of the spin cluster. We have self-constrained our calculations to the 1NN cases to understand the effect of the cluster formation on the exchange parameter J . In this study, diverse arrangements of three and four spin clusters are considered as shown in Figure 1. Figure 3(a) shows the distribution of J as a function of cluster size. The extra-circled points represent the case for the most energetically favorable geometry of the clustered spins. As can be seen from the figure 3(a), the exchange parameter J between two spin components of the spin cluster shows a strong dependence on the cluster geometry. As the size of the cluster increases, the variability of the exchange parameter J

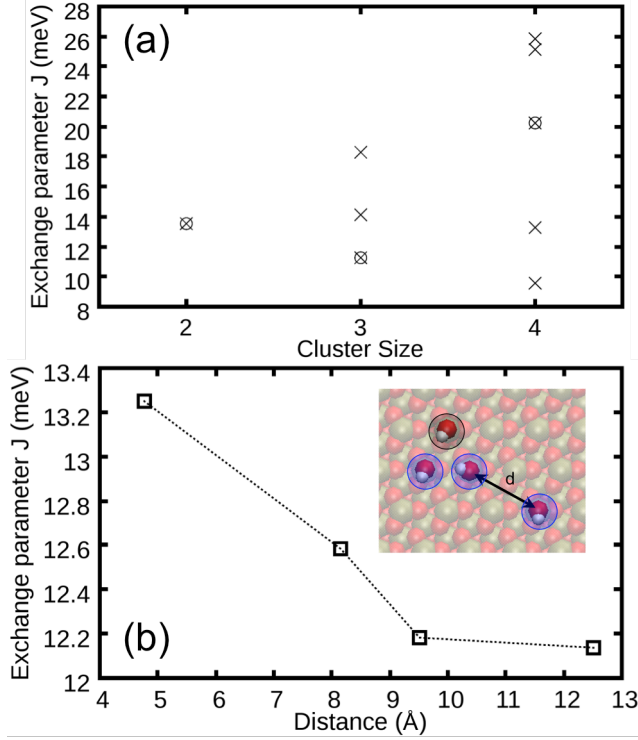


Fig 3. The effect of spin cluster on the exchange interaction parameter (J): (a) exchange interaction parameters as a function of size and shape of the cluster. (b) the effect of an additional spin on the exchange interaction of the spin cluster. The magnetic exchange interaction of the spin clusters can be affected by diverse conditions including geometry, size and nearby magnetic spins.

increases. For example, the exchange parameter J of the four spin clusters varies from 9.53 meV to 25.82 meV. Thus, the geometry of the spin cluster is another important factor to determine the magnetic coupling strength.

We further examine the effect of a neighboring spin on the exchange parameters J of the spin cluster. For the study, we again choose the case of the triangular spin cluster. Figure 3(b) shows the variation of J within the spin cluster in a vicinity of an additional spin. In-set figure shows the schematic view of the geometrical arrangements of the OH groups; blue and black circles represent the region where the magnetic moment is oppositely aligned under up antiferromagnetic condition. As can be seen, the existence of a neighboring spin enhances the exchange parameter J of the triangular cluster. The exchange parameter J is increased from 12.14 meV to 13.25 meV as an additional spin moves from 4NN to 1NN distance. Thus, the magnetic coupling strength of the spin cluster can also be affected by a neighboring spin.

Our study shows that the magnetic coupling strength can be affected by diverse factors including distance, clustering, geometry, and neighboring spins. We now focus on how the magnetic exchange interactions are affected by external stresses. Figure 4(a) shows the change of exchange coupling parameter as a function of two single-axis stresses into the slab; the direction parallel and perpendicular to two OHs arrangement. Negative and positive stresses represent compressive and tensile stress. In this study, only the 1NN arrangement is considered. As we can see from figure 4(a), the exchange parameter shows a strong dependence on both parallel and perpendicular directional stress. For the

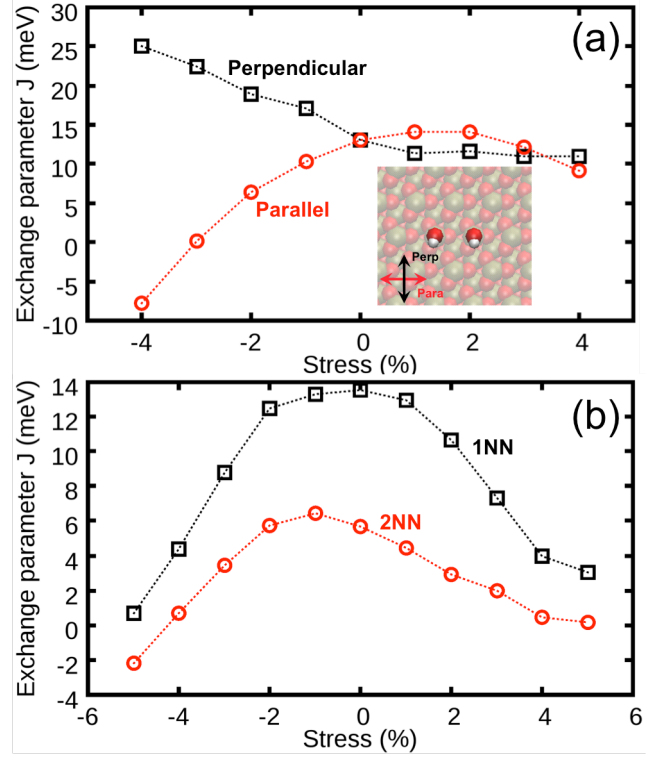


Fig 4. Variation of exchange interaction parameter (J) as a functional of (a) single-axis or (b) bi-axis stress. Parallel and perpendicular directions represent the direction of load compared to the arrangement of two OH groups.

compressive stress, parallel directional compression reduces the exchange parameter while the perpendicular directional compression enhances the exchange parameter. Our study shows that the exchange parameter of 1NN has been changed to -7.82 and 25.05 meV under 4% of parallel and perpendicular compressive stress. The negative sign represents the change of preferential alignment from ferromagnetic to antiferromagnetic. On the other hand, the tensile stresses only weakly affect the exchange parameter for both directions. For the parallel direction, the exchange parameter reaches the maximum of 14.11 meV under 1% tensile stress and gradually decreases to 9.11 meV under 4% tensile stress. Similarly, the perpendicular tension also reduces the exchange parameter to 10.99 meV with 4% tensile stress. Thus, an external stress can tune the exchange interaction between OH-induced magnetic moments.

We further look at the effect of bi-axial stresses on the magnetic exchange interaction. Figure 4(b) shows the variation of J as a function of bi-axial stress. As can be seen, both compressive and tensile bi-axial stresses have mainly reduced the exchange interaction for both 1NN and 2NN arrangements. These results are understandable since the single-axis stress showed that the reduction of J is more prominent than the increase of J . We note here that the combinatory effect of bi-axial compressive stress has slightly enhanced the exchange parameter of 2NN under 1% compressive stress. Nevertheless, our study clearly shows that the external bi-axial stress can significantly reduce the exchange interaction and induce a spin glass formation of the OH-induced surface magnetic moments. Thus, our study indicates that the external stress can be used to tune the

exchange interaction of OH-induced surface magnetic moments.

Finally, we searched for other surface modifications to enhance or degrade the spin-spin interactions. First, we added a He atom in-between two OH groups to elucidate the direct exchange component of the magnetic coupling. Our study shows that the addition of He will not affect the exchange coupling parameter indicating that the direct wave function overlaps between the two induced magnetic spins are unlikely and the exchange interactions between the spins are mainly originated from the indirect exchange interaction through the slab. On the other hand, the introduction of an Al vacancy between the spins enhances their interactions up to and beyond the 4NN.

Discussion

Our previous study showed that the anisotropic energy of the OH-induced surface magnetic spins is very small (~ 0.01 meV), indicating that the direction of surface spins can be easily changed at the surface.[13] The present results show that for an unstrained surface, the OH-induced surface magnetic moments are decoupled when their separation exceeds ~ 10 Å. This result explains the experimentally observed surface spin density of 5×10^{17} spins/m² (1 spin/200 Å²), which is essentially the upper bound of noninteracting surface spin density before the surface spins will form a spin cluster. Therefore, the actual surface spin density on sapphire could be higher than the experimentally reported value, since individual spins in a cluster are not resolved.

To understand the physical origin of the variance in magnetic exchange parameter under the different external stresses, we examined the electronic density of states (DOS). Figure 5(a) shows the difference in partial DOS (PDOS) of oxygen atoms contributing to surface magnetic spins near the Fermi level. Under the 5% compression, the occupied up-spin PDOS has shifted to lower energy level, while the unoccupied down-spin PDOS has shifted to higher in energy [see Fig. 5(a)]. In order to further understand how the shift of electronic density affects the magnetic coupling, we have employed the molecular orbital theory into the OH-induced surface magnetic spins; although OH-induced spin states are hybrids between oxygen p-orbitals, we can take the OH-induced spin state as an elementary unit. Then, the hybridization of the two spin states can create positive and negative states around E_F . If the direction of both spins is parallel, the energy of the two spin states will be identical (ferromagnetic alignment). If one of them is oppositely aligned, one spin state will have a higher energy state and the hybridization of the two spin states will be located below and above the E_F , as in Fig. 5(b). With the application of 5% compression, the occupied electronic states are shifted to lower energies and thus the antiferromagnetically aligned state become energetically more stable under the compression. That is the reason we observe the downward shift of the occupied PDOS along with the upward shift of the empty PDOS in Fig. 5(a). The compression stabilizes the antiferromagnetically aligned hybridized states by downshifting the energy level of the occupied states. This can be understood as a competition between double exchange-like mechanism and superexchange-like mechanism. While a double exchange-like mechanism

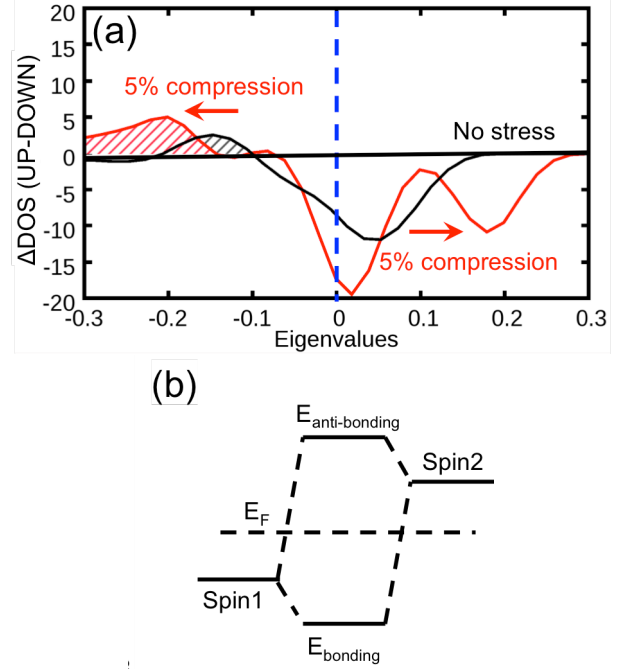


Fig 5. (a) Change in magnetization density near the Fermi level (set at 0 eV) for 2NN spin-spin exchange with and without compressive stress. (b) Schematic energy level diagram for interaction between non-degenerate spin states (e.g., antiparallel or misaligned spins in a magnetic field).

leads to a ferromagnetic ordering of OH-induced surface magnetic spins, a superexchange-like mechanism becomes dominant and antiferromagnetic coupling is more prominent under compression. As a result, the antiferromagnetic coupling component becomes energetically more stable under compression. On the other hand, tensile stress does not significantly modify the surface magnetic exchange interaction.

Summary

In summary, we have studied a variety of spin-spin interactions mediated by the surface, on a model system consisting of paramagnetic OH impurities on a (0001) sapphire surface, using density functional theory. We find the range of exchange interaction between spins to be ~ 10 Å for a relaxed surface, with the spins favoring ferromagnetic ordering. The interactions are “RKKY-like,” with the substrate mediating the exchange. The interaction is slightly enhanced for clusters of spins acting on a bare spin. In-plane compressive strain of the sapphire, in particular in the direction perpendicular to the line between two localized spins, enhances the exchange interaction. Tensile strain does not affect the spin-spin interaction significantly. Atomic defects between the spins, such as certain surface vacancy configurations, can greatly enhance the exchange interaction and range. The physical origin of the enhanced spin-spin interaction through the insulating substrate can be understood as “double exchange-like” when relaxed, with a “super exchange-like” mechanism becoming dominant under compressive stress. These results suggest an opportunity to tune the spin-spin interactions on the surface by engineering strain in the device.

Acknowledgements

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References

- [1] J. Q. You, and F. Nori, *Physics Today* **58**, 42 (2005).
- [2] J. Clarke, and F. K. Wilhelm, *Nature* **453**, 1031 (2008).
- [3] J. M. Martinis, *Quantum Information Processing* **8**, 81 (2009).
- [4] J. Zmuidzinas, *Annu. Rev. Cond. Mat. Phys.* **3** (1), 169 (2012).
- [5] B. A. Mazin *et al.*, *AIP Conf. Proc.* **605**, 309 (2002).
- [6] P. K. Day *et al.*, *Nature* **425**, 817 (2003).
- [7] D. R. Schmidt, C. S. Yung, and A. N. Cleland, *Appl. Phys. Lett.* **83**, 1002 (2003).
- [8] M. Hatridge *et al.*, *Phys. Rev. B* **83**, 134501 (2011).
- [9] F. C. Wellstood, C. Urbina, and J. Clarke, *Appl. Phys. Lett.* **50**, 772 (1987).
- [10] R. C. Bialczak *et al.*, *Phys. Rev. Lett.* **99**, 187006 (2007).
- [11] J. Bylander *et al.*, *Nature Physics* **7**, 565 (2011).
- [12] S. Sendelbach *et al.*, *Phys. Rev. Lett.* **100**, 227006 (2008).
- [13] D. Lee, J. L. DuBois, *Phys. Rev. Lett.* **112**, 017001 (2014).
- [14] J. Clarke, personal communication.